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Physical and Mathematical Modeling of Nitrification in a Lotic System

(U.S.) Environmental Research Lab, Athens, GA

1978

TECHNICAL REPORT DATA
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1. REPORT NO. EPA-600/J-78-066	2. JOURNAL ARTICLE	3. PB 289657
4. TITLE AND SUBTITLE: Physical and Mathematical Modeling of Nitrification in a Lotic System		5. REPORT DATE
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): J. L. Malanchuk, R. R. Lassiter, H. W. Holm, H. P. Kollig, and A. V. Quinlan		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Environmental Research Laboratory, U.S. Environmental Protection Agency, College Station Road, Athens, GA 30605		10. PROGRAM ELEMENT NO. 1LA760 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS: U.S. Environmental Protection Agency--Athens, GA, Environmental Research Laboratory, College Station Road, Athens, GA 30605		13. TYPE OF REPORT AND PERIOD COVERED: Proceedings article 14. SPONSORING AGENCY CODE: EPA/600/01

15. SUPPLEMENTARY NOTES
In: Microbiology-1978. D. Schlessinger (ed.). Washington, American Society for Microbiology. p. 380-383. 1978. Contact: R. R. Lassiter, 8-250-3162

16. ABSTRACT

A study of nitrification in a flowing experimental ecosystem was used to test a simple mathematical model. In the experiment, ammonia was introduced into the channel under varying flow and mixing conditions. Dissolved O_2 and CO_2, pH, and the inorganic nitrogen series (total ammonia, NO_2^-, and NO_3^-) were measured. The model assumed first order kinetics for transformation of the ammonia to NO_3^-. Stoichiometric coupling of nitrification was assumed. The model worked better for higher flows and turbulence levels and it was concluded that some of the simplifying assumptions that were not met were important at the low flow conditions.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Mathematical models Nitrogen Nitrification		12A 68D

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INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT: Release to Public	19. SECURITY CLASS (This Report): Unclassified 20. SECURITY CLASS (This page): Unclassified	21. NO. OF PAGES: 6 22. PRICE: PC A02 MF A01

EPA Form 2220-1 (9-73)

EPA-600/J-78-066
JOURNAL ARTICLE

Reprinted from MICROBIOLOGY 1978
1978
American Society for Microbiology

Physical and Mathematical Modeling of Nitrification in a Lotic System

J. L. MALANCHUK,[1] R. R. LASSITER, H. W. HOLM, H. P. KOLLIG, AND A. V. QUINLAN

Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia 30601, and Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

INTRODUCTION

Nitrification, the two-step oxidation of NH_4^+ to NO_3^- through an NO_2^- intermediate, is a key fragment of most cyclical pathways of nitrogen in the environment. In terrestrial systems, nitrification results in the formation of NO_3^-, which is readily leached through the soil profile and lost from terrestrial ecosystems. In aquatic systems, nitrification is important because of its potential for depleting dissolved O_2 supplies.

The primary objective of this study was to investigate whether a simple model conceptualization is sufficient to account for nitrification over a limited range of water flow and turbulence. A secondary objective was to collect rate data that will ultimately be related to channel surface area and volume. These objectives were pursued through the joint use of a spatially heterogeneous flowing microcosm and a mathematical model.

PHYSICAL MODEL

Description

Experiments were conducted in the Aquatic Ecosystem Simulator (AEcoS), an instrumented environmental chamber that houses a flow channel and provides control of air and water temperature, control of water flow and turbulence, control of light quality and quantity, and automatic measurement capability for dissolved materials, including the gases CO_2 and O_2 (1, 3, 5).

Freeman's reference water (2) was modified to contain 5 mg of NH_4^+-N per liter as the nitrogen source and a trace element mixture (8). Nitrifying organisms from pond sediment were cultured in chemostats and initially seeded into the channel.

[1] Present address: Institute for Man and Environment, State University of New York, Plattsburgh, NY 12901.

Observed Data

Experiments were conducted in a 3 × 3 arrangement for three flow rates and three turbulences at 25°C under low-level room light intensity and 50% relative humidity. Figure 1A illustrates steady-state $[NH_4^+]$ and $[NO_3^-]$ along the length of the channel at a flow rate of 1,892 liters/day. Two experiments were conducted independently of each other to check replicability at the turbulence provided by the paddlewheels rotating at 5 rpm. The results of the experiment conducted at the turbulence generated by a 2-rpm paddlewheel speed are also illustrated (Fig. 1A). The data for dissolved $[O_2]$ and $[CO_2]$ are presented in Fig. 1B for the same experiments, and observed pH is presented in Fig. 1C.

MATHEMATICAL MODEL

Conceptualization

The model is composed of five state variables (Fig. 2), one each for $[NH_4^+]$, $[NO_2^-]$, $[NO_3^-]$, $[O_2]$, and $[CO_2]$. Several major assumptions were made in the overall construction:

(i) NH_3 oxidation is a function of $[NH_4^+]$ and is, therefore, pH dependent.

(ii) NO_2^- oxidation is pH independent; that is, both NO_2^- and HNO_2 are available for oxidation.

(iii) Densities of populations oxidizing NH_4^+ and NO_2^- are uniform along the channel and, therefore, subsumed in rate coefficients.

(iv) Neither $[O_2]$ nor $[CO_2]$ is rate limiting and can be coupled stoichiometrically to the nitrification reaction rates.

The observed pH data are used to compute a distribution coefficient between alternative forms of carbon (6). The model assumes CO_2 to be the reactive species, and the CO_2 to total carbon ratio, α, is computed as

$$\alpha = 1 + \left\{ \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} \right\}^{-1}$$

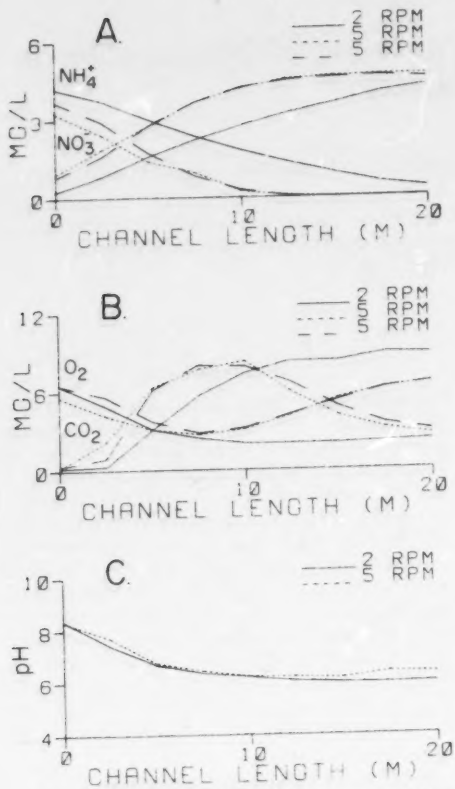

FIG. 1. *Replicates of steady-state concentrations of NH_4^+ and NO_3^- (A), O_2 and CO_2 (B), and observed pH (C).*

where $K_5 = 10^{-6.352}$ and $K_6 = 10^{-10.329}$. A similar approach is used to compute the ratio of NH_4^+ to total N, β. The β fraction is

$$\beta = 1 + \left\{\frac{5.71 \times 10^{-10}}{[H^+]}\right\}^{-1}$$

Regulation of O_2 consumed in NH_3 oxidation is by $[NH_T]$, and $[NO_2^-]$ governs the amount of O_2 consumed in NO_2^- oxidation. Stoichiometric coefficients s_1 and s_2, coupling O_2 utilization to NH_4^+ and NO_2^- oxidation, respectively, were assumed constant (4). Stoichiometric coefficients were also computed regulating CO_2 consumed in the growth of *Nitrosomonas*, s_4, based on the concentration of NH_4^+ oxidized, and of CO_2 consumed in *Nitrobacter* growth, s_5, based on NO_2^- oxidized (4).

Chemical transformations are described by a series of first-order, linear differential equations with constant coefficients as follows:

$$\frac{d[NH_T]}{dt} = -k_1[NH_4^+]$$

where

$$[NH_T] = [NH_3] + [NH_4^+]$$

$$\frac{d[NO_2^-]}{dt} = k_1[NH_4^+] - k_3[NO_2^-]$$

$$\frac{d[NO_3^-]}{dt} = k_3[NO_2^-]$$

$$\frac{d[O_2]}{dt} = k_2([O_2]_{sat} - [O_2]) - s_1k_1[NH_T] - s_2k_3[NO_2^-]$$

$$\frac{d[C_T]}{dt} = k_4([CO_2]_{sat} - [CO_2]) - s_4k_1[NH_T] - s_5k_3[NO_2]$$

where

$$[C_T] = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

The coefficients for NH_4^+ and NO_2^- oxidation are k_1 and k_3, respectively. The reaeration coefficients (k_2 and k_4) for O_2 and CO_2, respectively (7), are used to compute the gain or loss of gases to the atmosphere by multiplying the reaeration coefficient by the difference between the saturation value of the gas and the simulated concentration of the gas.

The chemical transformations occur as the flow proceeds along the channel length. Physical dispersion of the dissolved solute throughout the water also acts to distribute the chemical along the distance axis. Thus, the total equation describing mass transport of solute in

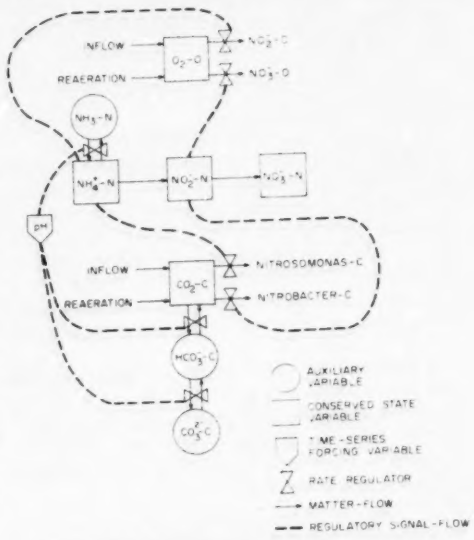

FIG. 2. *Conceptual model of nitrification in the Aquatic Ecosystem Simulator.*

one dimension incorporates a dispersal term and a flow term in addition to the terms describing the chemical transformations. The total equation describing the state variables is

$$\frac{\partial[N_i]}{\partial t} = \frac{D\partial^2[N_i]}{\partial x^2} - \frac{V\partial[N_i]}{\partial x} + S[N_i]$$

where $[N_i]$ is the concentration of the i^{th} species of chemical, t is time, x is distance, D is the coefficient of dispersion, V is the coefficient of velocity, and S is the source-sink term for chemical transformation.

Corroboration

Figures 3A and 3B represent a 96-h simulation versus observed steady-state data for an experiment conducted at 1,892 liters/day and a paddlewheel speed of 5 rpm. The rate coefficients for NH_4^+ and NO_2^- oxidation—k_1 and k_3, respectively—were adjusted during the range of rates observed within the experiment to obtain the simulated results (Fig. 3A and 3B). Agreement between simulated and observed data for dissolved O_2 and CO_2 (Fig. 3B) is not as accurate as for NH_4^+ and NO_3^- because emphasis in the modeling effort has been on the nitrogen transformations and not on dissolved O_2 and CO_2. Future modeling research will focus on improved prediction of dissolved gases.

A more severe test of the predictive power of the model was performed by a simulation of chemical dynamics at twice the flow and turbulence (Fig. 3C) but with no readjustment of chemical rate coefficients. A comparison of simulated versus observed data for $[NH_4^+]$ and $[NO_3^-]$ (Fig. 3C) indicates that the model is a good predictor of NH_4^+ and NO_2^- oxidation.

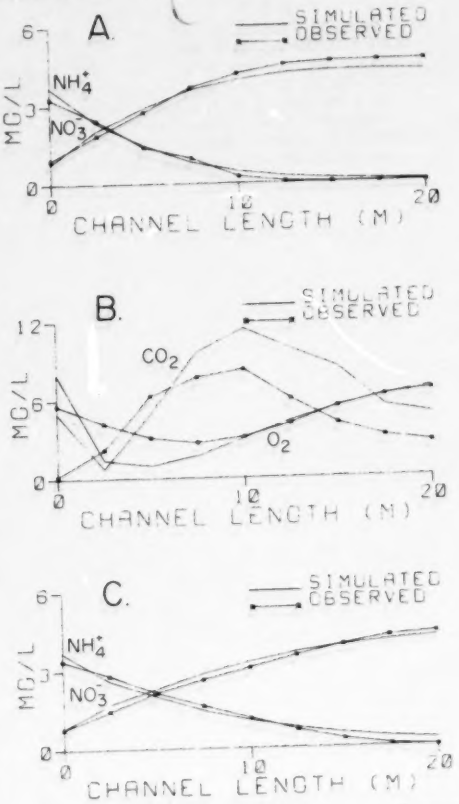

FIG. 3. *Comparison of simulated versus observed steady states at 1,892 liters/day and 5-rpm turbulence for NH_4^+ and NO_3^- (A) and for O_2 and CO_2 (B). Simulated versus observed steady states of NH_4^+ at twice the flow and turbulence are shown in C.*

CONCLUSIONS

A simple linear model with one set of rate coefficients accounts for nitrification in the AEcoS over a limited range of flow and turbulence. This degree of success is encouraging; however, the lack of complete success points out the necessity of further modeling work.

The range of success (high turbulence and flow levels) indicates the dominance of physical processes when transport of materials has ceased to be limiting. The range within which the model was less successful is that of low flow and turbulence, where it appears that nitrification is limited by the rate of delivery of dissolved gases and nitrogen substrates to the microbially active surface. In this range a model structure completely coupling gas concentration and reaction rate (rather than the one-way stoichiometric coupling) may be more useful than the simple linear model. Furthermore, the assumption concerning homogeneous population densities is probably not valid and mandates the inclusion of spatially varying rate coefficients.

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